# MINERAL MATTER EFFECTS IN COAL PYROLYSIS

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KEYWORDS: pyrolysis, coal, minerals

## INTRODUCTION

Coal pyrolysis is a fundamental first step in combustion processes [1]. Yet coals exhibit a wide variation in pyrolysis behaviors. The origins of these wide variations are, for a given set of experimental conditions, both structural and compositional in nature. Because of its thermochemical and catalytic properties, mineral matter plays an important role in both the thermodynamics (product mixes, activation energies) and kinetics of coal pyrolysis [2]. The issue is further complicated by the manner in which mineral matter is distributed in various coals. While many classifications are possible, grouping into three classes is most common [3]. These classes are: (1) discrete minerals such as clays, oxides (basic and acidic) and sulfides; (2) organometallic matter such as ion-exchangeable cations; and (3) dispersed trace elements and compounds. A considerable body of research exists for studying equilibrium and non-equilibrium effects of the various forms of coal minerals on coal combustion [4,5,6].

In the present paper the mineral matter effects on coal pyrolysis are being analyzed using an approach whereby observable spectroscopic (TG/MS) differences in the pyrolytic decomposition between fresh coal and demineralized coal are reconstructed from the sum of mineral matter effects on pyrolysis arising from adding back, singly and in pairs, individual minerals in various forms.

## EXPERIMENTAL TECHNIQUE

A low rank coal, Beulah Zap lignite was chosen because of its readily exchangeable cations, the strategic and technological importance of the huge Northern Great Plains lignite resource, and its availability as a standard reference coal through the Argonne National Laboratory Premium Coal Sample Program (ANL-PCSP).

Prior to sample preparation, coal is freezer stored under Ar or $N_2$ at -30 to -90 C so that oxidation is prevented. A standard HCl/HF acid wash is used to demineralize the coal. This has been shown not to alter coal structure [6], but does influence the number of reactive sites and surface reactivity in the coal [8,9].

Subsequently, cations and/or minerals are added back into the coal following demineralization. The cations are added using titration techniques and the sulfide or oxide minerals, as well as the clays, added by physical mixing. The titration results agree within +/- 10% of ICP/AES (Inductively Coupled Plasma/Atomic Emission Spectroscopy) determinations. Figure 1 shows the comparison of the titration ion concentration with the ICP/AES measurements.

Following sample preparation, pyrolytic decomposition is studied. Thermochemical kinetics are obtained using a home-built thermogravimetry/mass spectrometry (TG/MS) system [10] in conjunction

with PAS (photoacoustic spectroscopy) using an MTEC model 200 PAS cell and Perkin Elmer Model X1760 FTIR system. The yield of char or ash is quantified using TGA and mineral concentrations are quantified using ICP/AES. Data for each run are replicated three times, and a minimum of three heating rates per sample composition are run in order to evaluate the kinetic parameters using one of three statistical kinetic programs.

EXPERIMENTAL RESULTS

Sample Preparation-- Figure 2 demonstrates the effectiveness of the concentrated HF/HCl demineralization procedure. The ICP/AES data show that 95% of the mineral matter was removed. Furthermore, TG/MS data, as exemplified in Figures 3a and 3b, indicate that major structural transformations do not occur as a result of demineralization.

Minerals were subsequently added to the demineralized coal by physical mixing or by ion exchange titration. Figure 4 shows FTIR data including the computed difference between fresh (Figure 4a) coal and demineralized (Figure 4b) coal FTIR spectra. Figure 4c shows the difference between FTIR spectra for fresh Beulah Zap coal and demineralized Beulah Zap. The peaks at 1090 cm$^{-1}$ are particularly significant for cations and mineral phases. Note the strong similarities between the calculated difference spectrum in Figure 4c and the measured spectrum of ash obtained by low temperature ashing (Figure 4c). The effect of adding calcium is also given. The peaks for hydrogen replacement of cations and for the existence of mineral phases are consistent with known ion exchange and mineral substitution mechanisms.

Coal Pyrolysis - The effects of demineralization and of adding 2.6% Fe to demineralized Beulah Zap on specific products of devolatilization are shown in selected, time- and temperature-resolved mass spectral data in Figure 3.

Figure 3a-d shows the influence of demineralization (followed by adding iron chloride to demineralized coal) upon the DTG curve, the total ion count signal and the time (or temperature)-resolved ion profiles for $H_2^*$ (m/z 2), $CO^*$ (m/z 28), and $H_2O^*$ (m/z 18). The main features of the DTG profiles are replicated in the total ion count profiles. The mass spectral profiles for fresh and demineralized coal exhibit peak shifts in both temperature and amplitude. For iron, the concurrent sharp fall off of $H_2O$ accompanied by a sharp rise in $H_2$ (which is doubly activated) and CO is strongly suggestive of a water-gas-shift reaction. Moreover, the activation energies, based on first order kinetics, are similar for $H_2$ and CO. Both calcium and iron affect the hydrogen generation kinetics.

Kinetics - A number of kinetic parameter-fitting models were evaluated for devolatilization kinetic parameter determination. The techniques of Yun (1989) and Burnham (1989) [11,12] are specifically focussed on distributed activation energy models. However, not all the reactions are necessarily uncoupled parallel first order reactions. The apparent activation energies and reaction order may be estimated from leading edge or TG/MS line profiles. Table 1 shows the computed activation energies for $H_2$ and CO. The hydrogen generation curve may arise from a number of possible mechanisms. The experimental data for DMBZ+ 2.6% FeCl$_3$ are indicative of two distinct reactions. The apparent activation energy of 42.2 K cal/mole is apparently increased by the contribution of lower temperature reactions (water-gas-shift and main pyrolysis reaction).

The existence of catalytic effects of mineral matter is reinforced by the thermochemical kinetic data enumerated in Table II. The fresh Beulah Zap coal activation energy is the highest and hence pyrolysis proceeds at the fastest rate. The lowest activation energy is for demineralized Beulah Zap

coal, while the activation energies for demineralized Beulah Zap samples with added iron and calcium lie in between.

CONCLUSIONS

Marked effects of iron and calcium cation content on the hydrogen, water, and carbon monoxide generation rates during pyrolysis were observed. In addition, the potential for PAS-FTIR spectroscopy in quantitative applications to coal spectra was demonstrated on fresh demineralized and remineralized coal. Demineralization and selected remineralization affect the rate of gas evolution in general and of hydrogen and carbon monoxide in particular. This is in good agreement with published literature data [13,14,15].

ACKNOWLEDGEMENTS

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TABLE I
ACTIVATION ENERGIES FOR HYDROGEN AND CO

| Coal Sample* | Mass Peak | Activation Energy (kcal/mol) | Observed Temp. Range (K) |
|---|---|---|---|
| FRBZ | m/z 2 ($H_2$+) | 36.8 | 800-1200 |
| | m/z 28 (CO+) | 22.7 | 800-1200 |
| DMBZ + 2.6% Fe | m/z 2 ($H_2$+) | 42.2 | 800-900 |
| | m/z 28 (CO+) | 35.2 | 800-1200 |

* FRBZ = Fresh Beulah Zap
  DMBZ = Demineralized Beulah Zap

TABLE II
ACTIVATION ENERGIES BASED ON TG WEIGHT LOSS DATA

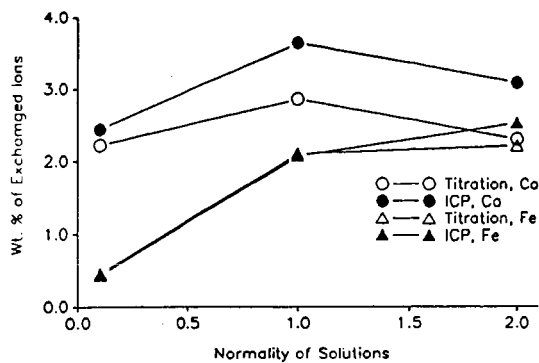| Coal Sample* | Ea (kJ/mol) | Chosen % Conversion | Heating Rate Used |
|---|---|---|---|
| FRBZ | 213 $\pm$ 43.68 | 30, 32, 34, 36, 38, 40 | 5, 10, 25, 50 |
| DMBZ | 102.79 $\pm$ 32.72 | 15, 18, 21, 24 | 5, 10, 25 |
| DMBZ + Fe | 131.94 $\pm$ 51.40 | 30, 32, 34, 36, 38 | 10, 25, 50 |
| DMBZ + Ca | 144.44 $\pm$ 40.67 | 30, 32, 34, 36, 38, 40 | 10, 25, 50 |

* see Table I

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Figure 1. Ion exchange was accomplished via titration and verified by ICP/AES. The iron substitution data are nearly identical, indicating a more effective exchange than for calcium. The concentration in the coal tends to saturate above 1N solutions.
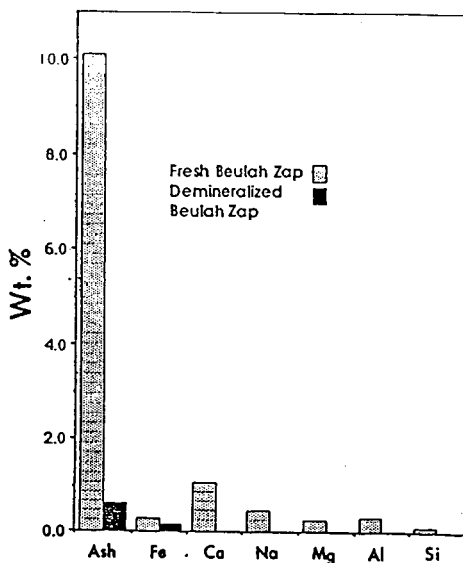


Figure 2. ICP-AES data for fresh and demineralized Beulah Zap coal. While the efficiency for mineral removal varies by element, the demineralization is seen to remove about 95 percent of the total mineral matter.
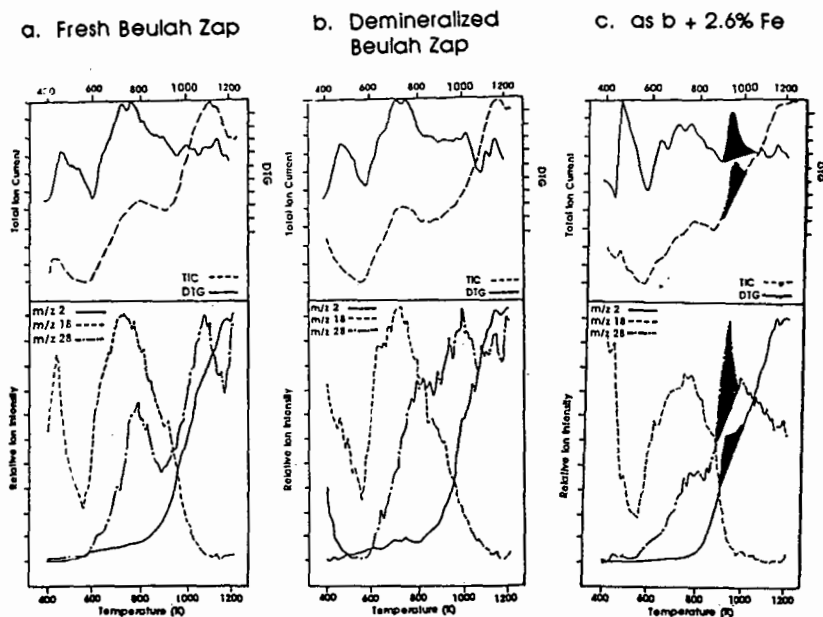
Figure 3. Selected thermogravimetric weight loss, total ion count and mass spectral profiles for $H_2O$, CO and $H_2$ is demineralized and remineralized Beulah Zap coal. Of note are the duplication of the main DTG features in the total ion count and the evidence in Figure 4c (see shaded areas) of water-gas-shift reactions (falling water concentration with concurrently rising hydrogen and CO concentrations). The iron cations shift the hydrogen profile to lower temperatures with accompanying rapid rise in CO. The activation energies for $H_2$ (m/z 2) in Table I are indicative of two interacting reactions for hydrogen generation, e.g., water-gas-shift and crosslinking.
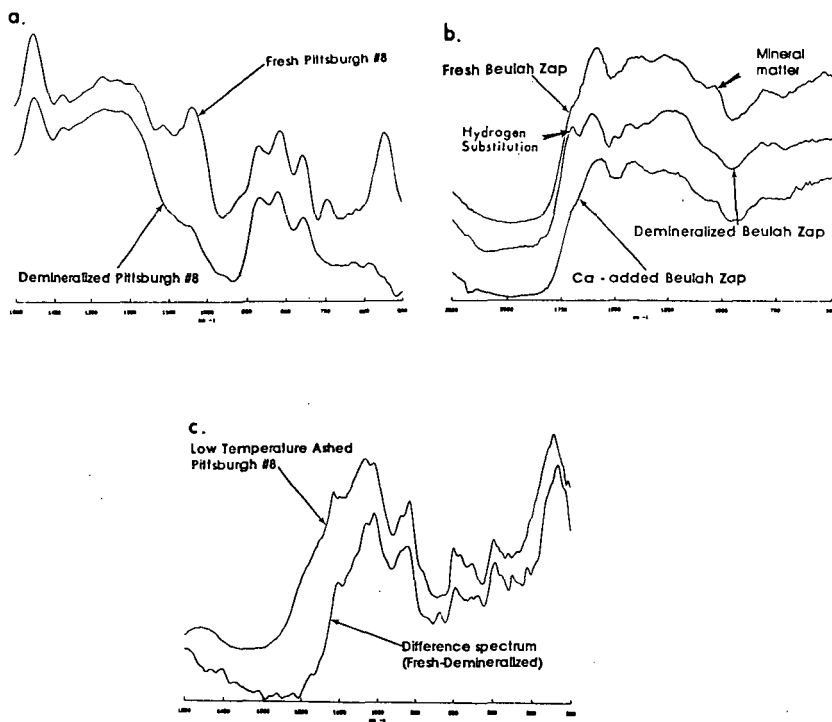
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Figure 4. Photoacoustic FTIR spectra for fresh and demineralized Pittsburgh #8 and Beulah Zap coals. Of particular note in Figure 4a and c are the strong similarities between the computer difference spectra (between fresh and demineralized coal) and the ash spectra. Figure 4b shows the verification of calcium ion exchange in Beulah Zap coal through the FTIR spectral shifts at 1690 $cm^{-1}$ and 1050 $cm^{-1}$ between fresh, demineralized and Ca-added coals.